Small-Scale Survey on the Contamination Status of Butyltin Compounds in Seafoods Collected from Seven Chinese Cities

Qun-fang Zhou, Gui-bin Jiang,* and Ji-yan Liu

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

Tributyltin (TBT) and its degradation products, dibutyltin (DBT) and monobutyltin (MBT), in the commercial sea products collected from seven Chinese cities were measured to evaluate the extent of contamination and the potential adverse effect on health. Universal existence of butyltins was found in these samples, and the concentrations of TBT ranged from <6.9 to 17175 ng of Sn g^{-1} of wet weight. The accumulation ratios of the pollutant in these organisms were as high as 10^3 or more compared with the previously reported data in corresponding water. The existing different accumulation capabilities of pollutants among the various seafood species were studied. It was observed that the butyltin compounds were comparatively stable during cooking or processing procedures in the manner of usual Chinese cooking way. The occurrence of butyltin compounds in sea products indicated a potential danger for the health of people who consumed seafood in these areas.

Keywords: *Butyltins; GC-FPD; seafood*

INTRODUCTION

It is well-known that tri-*n*-butyltin (TBT) has been in wide-scale application as a biocide, especially as a component in antifouling paints for ships (*1*). Flaking off of these paints from ship hulls and other factors such as absorption by organic and inorganic particles and subsequent deposition in the sediment contribute to environmental contamination by tributyltin and its derivatives, especially in areas of heavy boating and shipping traffic (*2*). Bioconcentration factors ranging from 10^2 to 10^4 have been determined for various aquatic species including fish, crustaceans, and algae (*3*−*6*). TBT will directly affect human health as many of oceanic organisms are consumed as delicious foods. Accordingly, it is of much interest to investigate the butyltin compounds in commercial sea products and the effects of cooking or processing procedures on the butyltins concentrations.

The present paper provides small-scale investigation results of several kinds of commercially available seafood collected from seven Chinese cities. Butyltin compounds contamination at levels of <19.8−18007 ng of Sn g^{-1} (mean = 408 ng of Sn g^{-1}) was found in these sea products by using the method of Grignard propylation and subsequently analyzed by using capillary GC-FPD with quartz surface-induced tin emission.

MATERIALS AND METHODS

Instrumentation. A GC-9A gas chromatograph (Shimadzu) was used throughout the experiment. A fused silica capillary column coated with a film of 0.17 μm (HP-1; 25 m × 0.32 mm i.d.) and a temperature program of 100 °C (hold for 1 min) to 150 °C (hold for 3 min) at 5 °C/min offered a baseline separation of all butyltin compounds. Nitrogen with high purity served as carrier gas and was kept at a pressure of 0.26 mPa on the column head. All of the analytes were detected by a laboratory-made flame photometric detector using quartz surface-induced luminescence (QSIL-FPD). The configuration and analytical figure of merits of this system were reported in detail in our previous publications (*7*, *8*). Detection was performed in a hydrogen-rich flame mode, and the flow rates of hydrogen and air were controlled at 260 and 90 mL/min, respectively. The measurement was carried out by using a 394 nm interference filter. The temperatures of the injector and detector were set at 220 and 160 °C, respectively. An SC-1100 PC data processing system recorded all of the chromatograms.

Reagents. Tetrabutyltin (TeBT, 96%), tributyltin chloride (TBT, 90%), dibutyltin dichloride (DBT, 97%), and monobutyltin trichloride (MBT, 97%) were obtained from Acros Organics. TeBT was used as an internal standard (IS). The stock solutions were prepared directly by dissolving the weighed TeBT, TBT, DBT, and MBT into methanol to form a concentration level of 1 mg/mL (as Sn), respectively, and the pH was adjusted to 2 with concentrated HCl to ensure its stability. All of the stock solutions were proved to be stable for at least 3 months in this way. Working standard solutions were freshly made by gradually diluting the corresponding stock solutions into deionized water. All of the solutions were stored at 4 °C in the dark.

The Grignard reagent of *n*-propylmagnesium bromide (*n*-PrMgBr, 2.0 M) was laboratory-prepared according to the standard synthetic methods (*9*).

All solvents and reagents used were of analytical reagent grade or better.

Glassware was rinsed with deionized water, decontaminated overnight in a 1:1 nitric acid solution, and then rinsed again.

Sampling. Figure 1 shows the sampling cities of sea organisms. These cities are located from southeast China to northeast China, where industries and fish culture are relatively highly developed and heavy environmental pollution might have been suffered in the aquatic systems. These aquatic products, which were digested directly as the seafood by the native citizens and the tourist guests, included some kinds of snails and shellfish and small amounts of fish, shrimp, and crab. They were mostly bought commercially from local retail markets. All of the samples were produced in the native places, except those of Beijing, which mostly came from

* Corresponding author (fax 8610-62923563; telephone 010-62849124; e-mail gbjiang@mail.rcees.ac.cn).

10.1021/jf010438y CCC: $20.00
Published on Web 08/14/2001

Figure 1. Map of sampling cities.

Tianjin, Qingdao, and Yantai. Most of the samples were bought shelled and crude, although a few were unshelled and artifactitious. All of the samples were kept frozen until analysis.

Procedure. Analyses for tri-, di-, and monobutyltin (TBT, DBT, and MBT) were carried out in 2 g (wet weight) of homogenized tissue of the unshelled sea products. After the tissue was mixed with 0.3 mL of the internal standard, TeBT (2 μg/mL), 10 mL of a THF−HCl (11:1) solution was added to convert all of the analytes to their corresponding chlorides. They were then extracted with 25 mL of 0.01% tropolone−hexane and 10 mL of hexane solution in turn under vigorous shaking for 40 and 10 min, respectively. The combined hexane extracts were concentrated to 2−3 mL by a rotary evaporator at 25 °C and then submitted to a Grignard propylation step without further treatment. The presence of traces of water in these extracts did not interfere with the propylation of butyltins to propylated compounds whenever an excess of (*n*-Pr)MgBr was added [1 mL of a 2.0 M solution of (*n*-Pe)MgBr in ether] (*10*). The mixture was shaken at room temperature for 15 min, which was enough for the complete reaction. It was subsequently treated with 5 mL of a 0.5 M H_2SO_4 solution to destroy the excess of Grignard reagent, followed by an extraction with 20 mL of hexane and an additional wash with ~40 mL of deionized water. After manual shaking for 5 min, the solution was allowed to stand for phase separation. The organic layer, containing the compounds of interest, was separated and concentrated to 1 mL and then dried and purified by anhydrous $NaSO_4$ (2 g) and Florisil (1 g), which had been packed in a Pyrex tube and prewashed with 10 mL of hexane. Another portion of hexane (10 mL) was let into the column to elute the analytes. The eluted solution was gently concentrated to 1 mL by passing a nitrogen stream. A 1 μL volume of solution was then injected into the GC for analysis.

The propylated standards were obtained by spiking suitable amounts of butyltins (MBT, DBT, and TBT) and the internal standard (TeBT) into the blank tissue and subsequently carrying out the same procedure described above. A sample blank was processed to ensure against background contamination at the low concentration during these experiments. Butyltin concentrations were calculated by peak height response relative to that of the internal standard, TeBT. The method was validated by the determination of 0.1 g of a certified reference material (CRM 477) in the same procedure.

RESULTS AND DISCUSSION

Evaluation of the Analysis Procedure and Quality Control. The whole process described above was based on a number of publications (*11*−*14*). Its reliability for butyltin analysis was confirmed by the satisfactory results offered by the determination of CRM 477. Table 1 shows the comparison of the certified values and the determined ones of the butyltins. It was clear that this method provided a precision of analysis of <8.7% for five replicates, and the recoveries of MBT, DBT, and TBT were 88.7, 98.7, and 107.3%, respectively, which were obtained by dividing the determined value by the corresponding certified value. The minimum detectable concentrations were 6.9 ng/g for TBT, 5.2 ng/g for DBT, and 7.8 ng/g for MBT, respectively. All of the results above proved the feasibility and high sensitivity of the whole analysis procedure including the preparation, separation, and detection of the analytes. It could be used confidently in extend butyltin analysis of the organisms.

Table 1. Results of the Determination of Butyltins in Certified Reference Material CRM 477

compd	certified value[a] (μg/g as compd)	determined value[b] (μg/g as compd)
MBT	1.50 ± 0.28	1.33 ± 0.11
DBT	1.54 ± 0.12	1.52 ± 0.13
TBT	2.20 ± 0.19	2.36 ± 0.20

[a] The dried mussel reference material was recertified in 1998 and the concentrations expressed as tribuyltin [TBT; $Sn(C_4H_9)_3^+$], dibutyltin [DBT; $Sn(C_4H_9)_2^+$], and monobutyltin (MBT; $SnC_4H_9^+$). [b] $n = 5$.

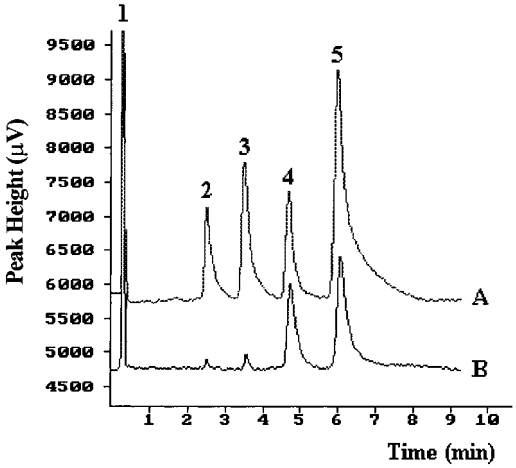

Figure 2. GC-FPD chromatogram of propylated butyltin standards (A) and a sample (*Chlamys farreri* collected in Dalian) (B). Peaks: 1, solvent (hexane, 1 μL); 2, $BuSnPr_3$, 50 pg as Sn; 3, Bu_2SnPr_2, 50 pg as Sn; 4, Bu_3SnPr, 50 pg as Sn; 5, internal standard Bu_4Sn, 60 pg as Sn.

Butyltin Analysis in the Seafood. The gas chromatograms of the propylated butyltin standards and a typical bivalve sample are shown in Figure 2. The response of the FPD was selective for Sn. Each compound of interest in the sea organisms was identified according to the retention time of the standards. Quantitative analysis was carried out according to the internal standard method. The concentrations of TBT, DBT, MBT, and the total butyltin (sum of TBT, DBT, and MBT) for all of the samples are reported in Table 2. Concentrations were given as Sn to allow direct comparison of the three kinds of butyltin species. The butyltin compounds, especially TBT, were found to widely exist in all of the samples except *Hemigrapsus penicillatus*, which was collected in Tianjin. The concentrations of total butyltin range from the limit of quantitation (<19.8) to 18007 ng of Sn g^{-1} (mean = 408 ng of Sn g^{-1}). The concentrations of TBT, DBT, and MBT ranged from <6.9 to 17175 ng Sn g^{-1}, from <5.2 to 692 ng Sn g^{-1}, and from <7.8 to 140 ng Sn g^{-1}, respectively (Table 2). The concentration of TBT accounts for 45−100% of the total butyltin concentration (mean = 95%). As the previous paper (*15*) showed that the mean contamination levels of butyltin in the corresponding water samples ranged from 0.11 to 0.68 ng of

Table 2. Concentrations (Nanograms of Sn per Gram) of Butyltin Compounds in Commercial Sea Organisms of China

sampling site	species	no.	sample name	MBT	DBT	TBT	total tin
Beijing	bivalves	1	*Mytilus galloprovincialis* (Lamarck, 1819)	16.9	58.6	142.7	218.2
		2	*Meretrix meretrix* (Linnaeus, 1758)	nd	nd	24.3	24.3
		3	*Scapharca broughtonii* (Schrenck, 1867)	nd	7.2	38.9	46.1
		4	*Macoma praetexta* (Martens, 1865)	nd	nd	22.8	22.8
		5	*Ruditapes philippinarum* (Adams et Reeve, 1850)	nd	nd	31.3	31.3
		6	*Chlamys farreri* (Jones et Preston, 1904) (crude)	nd	nd	31.6	31.6
			Chlamys farreri (Jones et Preston, 1904) (processed)	nd	nd	24.6	24.6
		7	*Cyclina sinensis* (Gmelin, 1790)	nd	nd	21.5	21.5
		8	*Ostrea (Ostrea) denselamellosa*(Lischke, 1869)	nd	nd	41.4	41.4
		9	*Macoma incogrua* (Martens, 1865)	17.8	8.9	21.5	48.2
	others	10	*Solen gouldii* (Conrad, 1867)	nd	nd	26.4	26.4
		11	*Auxis tapeinosoma* (Bleeker, 1854)	nd	nd	31.2	31.2
		12	Trichiurus haumela (Forskål, 1775)	nd	nd	25.9	25.9
Dalian	bivalves	13	*Ostrea (Crassostrea) talienwhanesis* (Crosse, 1862)	nd	nd	30.9	30.9
		14	*Chlamys farreri* (Jones et Preston, 1904)	20.5	27.6	410.1	458.2
		15	*Scapharca broughtonii* (Schrenck, 1867)	nd	nd	32.7	32.7
		16	*Laternula limicola* (Reeve, 1863)	140.1	692.1	17175.0	18007
	snails	17	*Natica clausa* (Broderip et Sowerby, 1829)	nd	nd	45.04	45.04
Qinhuangdao	bivalves	18	*Mytilus galloprovincialis* (Lamarck, 1819)	23.4	21.1	74.5	119.0
Tianjin	bivalves	19	*Mytilus ednlis* (Linnaeus, 1758)	nd	nd	33.7	33.7
		20	*Mytilus galloprovincialis* (Lamarck, 1819)	nd	34.7	65.7	100.4
		21	*Cyclina sinensis* (Gmelin, 1790)	nd	nd	35.9	35.9
Tianjin	bivalves	22	*Chlamys farreri* (Jones et Preston, 1904)	nd	nd	92.3	92.3
	snails	23	*Neptunea cumingi* (Crosse, 1862)	nd	nd	30.3	30.3
		24	*Natica fortunei* (Reeve, 1855)	nd	nd	32.0	32.0
		25	*Harpa conoidalis* (Lamarck, 1818)	nd	nd	27.1	27.1
	others	26	*Hemigrapsus penicillatus* (de Haan, 1835)	nd	nd	nd	
		27	*Acanthomysis koreana* (Ii, 1964)	nd	nd	31.4	31.4
Qingdao	bivalves	28	*Ruditapes philippinarum* (Adams et Reeve, 1850)	nd	nd	22.0	22.0
		29	*Ostrea (Crassostrea) gigas* (Thunberg, 1793)	9.2	14.7	180.8	204.7
		30	*Chlamys farreri* (Jones et Preston, 1904)	8.2	12.1	152.0	172.3
		31	*Solen grandis* (Dunker, 1858)	nd	nd	27.9	27.9
	snails	32	*Rapana venosa* (Valenciennes, 1846)	nd	nd	23.3	23.3
		33	*Natica clausa* (Broderip et Sowerby, 1829)	nd	nd	20.5	20.5
		34	*Eulima bilineata* (H. et A. Adams, 1858)	nd	nd	19.8	19.8
		35	Neverita ampla (Philippi, 1848)	nd	nd	29.4	29.4
		36	*Neverita didyma* (Röeding, 1798)	nd	nd	22.2	22.2
	others	37	Engraulis japonicus (Temminck et Schlegel, 1846)	nd	nd	22.3	22.3
Yantai	bivalves	38	*Chlamys farreri* (Jones et Preston, 1904)	nd	nd	63.8	63.8
		39	*Solen gouldii* (Conrad, 1867)	nd	nd	32.6	32.6
		40	*Ruditapes philippinarum* (Adams et Reeve, 1850)	nd	nd	70.0	70.0
		41	*Mytilus galloprovincialis* (Lamarck, 1819) (crude)	nd	nd	23.8	23.8
			Mytilus galloprovincialis (Lamarck, 1819) (cooked)	nd	nd	25.6	25.6
	snails	42	*Chlorostoma rusticum* (Gmelin, 1791) (crude)	nd	nd	28.2	28.2
			Chlorostoma rusticum (Gmelin, 1791) (cooked)	nd	nd	20.2	20.2
		43	*Neverita ampla* (Philippi, 1848)	nd	5.3	58.1	63.4
		44	*Rapana venosa* (Valenciennes, 1846)	nd	nd	24.4	24.4
		45	*Neptunea cumingi* (Crosse, 1862)	10.3	nd	21.7	32.0
	others	46	*Muraenesox cinereus* (Forskål, 1775)	nd	nd	29.6	29.6
		47	Engraulis japonicus (Temminck et Schlegel, 1846)	nd	nd	42.6	42.6
Lianyungang	bivalves	48	*Ostrea (Ostrea) denselamellosa* (Lischke, 1869)	nd	nd	29.9	29.9
		49	*Meretrix meretrix* (Linnaeus, 1758)	22.9	51.0	367.9	441.8
		50	*Silipua pulchella* (Dunker, 1858)	nd	nd	24.6	24.6
		51	*Macoma incogrua* (Martens, 1865)	nd	nd	35.1	35.1
	snails	52	*Neptunea cumingi* (Crosse, 1862)	nd	6.0	31.3	37.3

Sn g^{-1}, a mean accumulation ratio of the sea organisms $>10^3$ was observed by rough evaluation.

There existed a great difference among the mean butyltin contamination levels of the seafood in these places, which is clearly depicted in Figure 3. The pollution of butyltins in the Dalian seafood was most serious of all, and the contamination level was ~30−100 times as much as the others. *Laternula limicola* accumulated extremely high levels of butyltin, especially for TBT. It was supposed that this kind of sample was collected from an extremely polluted area, such as a shipyard or port where many ships berthed and there was a stronger potential of contamination of TBT from the antifouling paints. It was also suggested that the butyltin accumulation capability of this species might be particularly high. Subsequently, the pollution levels of the seafood collected in Qinhuangdao and Lianyungang were second greatest, and the contamination levels were both at a 10^2 order of magnitude. The rest, including those of Beijing, were comparatively less polluted and were all at the same order of magnitude. Accordingly, the results from the seafood collected in Beijing well corresponded with their sources. Although the mean butyltin contaminations in the water samples of these cities were almost at the same level, great differences existed between water samples collected at

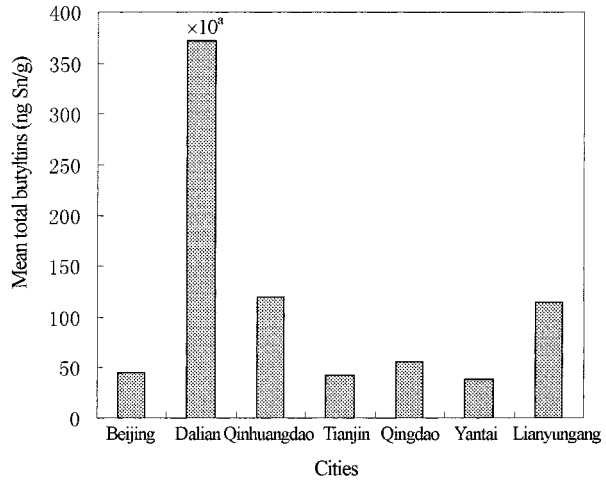

Figure 3. Comparison of the mean butyltin levels in seafood from different Chinese cities. [a]The mean butyltin level of Dalian seafood was 3715 ng of Sn g^{-1}.

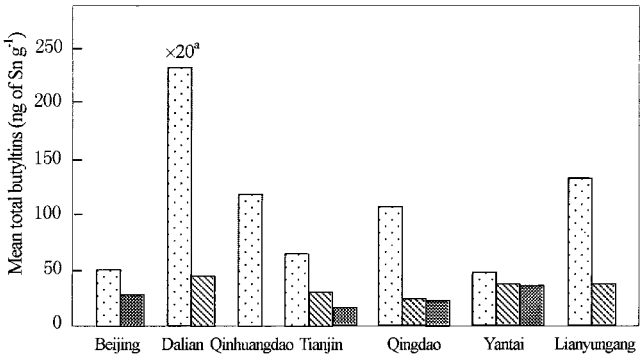

Figure 4. Comparison of the mean butyltin levels in different species in each city: (dotted bars) shellfish; (slashed bars) snails; (cross-hatched bars) others. [a]The mean butyltin level of Dalian shellfish was 4632 ng of Sn g^{-1}.

different sites in the same city (*15*). The butyltin contamination varied greatly with the different organism samples collected in the same cities as Table 2 shows. As the seafood products herein were commercially obtained in the market, it was hard to distinguish the detailed sites where they were collected. Thus, on the basis of the analysis above, we might presume that high butyltin contamination levels of the environment could lead to the high accumulation of butyltins in the organisms living there. Above all, the pollution of butyltin compounds in Dalian was most serious.

According to the results shown in Table 2, it was also easy to find that the accumulation capability of butyltin compounds also varied with the different organism species. If we divided all of the collected samples into three groups (bivalve, snail, and other species, which included fish, shrimp, and crab), we could then find that the mean concentration of total butyltins in bivalve species was obviously higher than that in the other two groups in every city. This result was clearly shown in Figure 4. So it might be presumed that the butyltin accumulation capability of bivalve species was much stronger than that of snail species or other collected organisms.

The effects on the butyltin concentrations by cooking and processing were also studied in a small scale. The usual seafood cooking method among Chinese people is to quickly pass the seafood through hot water in order to preserve the natural delicious taste of the food, and we adopted a similar experiment to determine the concentration variation of butyltins during the cooking process. According to the results of samples 41 and 42 shown in Table 2, there was no obvious difference in the butyltin concentrations between the crude and the cooked foods. The processing procedure might usually include unshelling, washing, addition of additives, and freezing. The comparison of sample 6 also showed no obvious differences existing in the butyltin concentrations before and after processing. Thus, it might be concluded that butyltin compounds would not degrade or be destroyed after being cooked or processed by the usual treatment described above.

There have been many reports about the environmental toxic impact of butytltin compounds, especially TBT, on sensitive marine organisms (*16*−*19*). It was also found that organotin compounds could induce immunotoxicity, neurotoxicity, skin and eye irritation, mutagenicity, and carcinogenicity in mammals (*20*). No study has been carried out on the deleterious chronic effects on human beings because of sampling difficulties. Maybe human resistance is strong, and there have been no obvious symptoms appearing under these chronic levels of exposure. However, two striking organotin poisoning accidents have occurred that could firmly prove organotins' acute toxicities to human beings. One was known as the "Stalinon" affair, and the other happened in China during the New Year's days of 1999 due to the consumption of methyltin-contaminated lard (*21*, *22*). We found that at high levels organotin compounds could cause people to feel sick, with symptoms such as dizziness, nausea, or even death. Accordingly, the health of the people who fed on the polluted seafood for a long period was of concern because of the universality of butyltins' existence in the seafood from these cities in China. Because of accumulation and biomagnification of the pollutants, it would appear that there could be deadly effects in the long term. Consequently, effective action should be taken as soon as possible.

CONCLUSIONS

This small-scale survey of seafood collected in seven Chinese cities demonstrated the universal occurrence of different degrees of butyltin contamination, of which the highest were found in Dalian's *Laternula limicola* (Reeve, 1863). A mean accumulation ratio of the sea organism $>10^3$ was observed by rough evaluation. Bivalve species might have greater accumulation capabilities of pollutants than the snails and other species studied herein. No obvious degradation or destruction of the butyltins was observed after cooking or processing according to usual Chinese methods. In view of the health of those people who regularly consume seafood, effective government action should be encouraged.

ACKNOWLEDGMENT

We greatly appreciate professor F. C. Adams for his kindly offering CRM477.

LITERATURE CITED

(1) Piver, W. T. Organotin compounds: industrial applications and biological investigation. *Environ. Health Perspect.* **1973**, *4*, 61−79.

(2) Maguire, R. J.; Tkacz, R. J.; Chau, Y. K.; Bengert, G. A.; Wong, P. T. S. Occurrence of organotin compounds in water and sediment in Canada. *Chemosphere* **1986**, *15*, 253−274.

(3) Hall, L. W., Jr.; Pinkney, A. E. Acute and sublethal effects of organotin compounds on aquatic biota: an interpretative literature evaluation. In *Critical Reviews in Toxicology*; Goldberg, L. Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 14, pp 159−207.
(4) Evans, D. W.; Laughlin, R. B.; Accumulation of bis-(tributyltin)oxide by the mud crab, *Rhithropanopeus harrisii*. *Chemosphere* **1984**, *13*, 213−219.
(5) Ward, G. S.; Cramm, G. C.; Parrish, P. R.; Trachman, H.; Slesinger, A. Bioaccumulation and chronic toxicity of bis(tri-*n*-butyltin)oxide (TBTO): tests with a saltwater fish. In *Aquatic Toxicology and Hazard Assessment*; Branson, D. R., Dickson, K. L., Eds.; American Society for Testing and Materials: Philadephia, PA, 1981; pp 183−200.
(6) Maguire, R. J.; Wong, P. T. S.; Rhamey, J. S. Accumulation and metabolism of tri-*n*-butyltin cation by a green alga, *Ankistrodesmus falcatus*. *Can. J. Fish Aquat. Sci.* **1984**, *41*, 537−540.
(7) Jiang, G. B.; Ceulemans, M.; Adams, F. C. Optimization study for the speciation analysis of organotin and organogermanium compounds by on-column capillary gas chromatography with flame photometric detection using quartz surface-induced luminescence. *J. Chromatogr.* **1996**, *727* (1), 119−129.
(8) Jiang, G. B.; Xu, F. Z. Analysis of butyltin species in water by gas chromatography with flame photometric detection using quartz surface-induced tin emission. *Appl. Organomet. Chem.* **1996**, *10*, 77−82.
(9) Zhou, Q.; Jiang, G.; Qi, D. Synthesis and application of propylmagnesium bromide Grignard reagent in derivatization of butyltin compounds. *Chinese J. Anal. Chem.* **1999**, *27*, 1197−1199
(10) Meinema, H. A.; Tineke, B. W.; Gerda, V. de Haan; Gevers, E. Ch. Determination of trace amounts of butyltin compounds in aqueous systems by gas chromatography/mass spectrometry. *Environ. Sci. Technol.* **1978**, *12*, 288−293.
(11) Rice, C. D.; Espourteille, F. A.; Huggett, R. J. Analysis of tributyltin in estuarine sediments and oyster tissue, *Crassostrea virginica*. *Appl. Organomet. Chem.* **1987**, *1*, 541−544.
(12) Takahashi, S.; Mukai, H.; Tanabe, S.; Sakayama, K.; Miyazaki, T.; Masuno, H. Butyltin residues in livers of humans and wild terrestrial mammals and in plastic products. *Environ. Pollut.* **1999**, *106*, 213−218.
(13) Kumiko, S.; Takashi, I.; Takashi, S.; Yukio, S. Determination of tri-*n*-butyltin and di-*n*-butyltin compounds in fish by gas chromatography with flame photometric detection. *J. Assoc. Off. Anal. Chem.* **1988**, *71*, 360−363.
(14) Bernardo, G. R.; Terry, L. W.; Gregory, G. S.; James, M. B. Butyltin concentrations in oyster from the gulf of mexico from 1989 to 1991. *Environ. Pollut.* **1993**, *81*, 103−111.
(15) Jiang, G. B.; Liu, J. Y.; Yang, K. W. Speciation analysis of butyltin compounds in Chinese sea water by capillary gas chromatography with flame photometric detection using in-situ hydride derivatization followed by headspace solid-phase microextraction. *Anal. Chim. Acta* **2000**, *421*, 67−74.
(16) Alzieu, C.; Héral, M.; Thibaut, Y.; Dardignac, M. J.; Feuillet, M. Influence des peintures antisalissures sur la calcification de la coquille de l'huître *Crassostrea gigas*. *Rev. Trav. Inst. Peches Marit.* **1982**, *45*, 101−106.
(17) Judith, S. W.; Jamie, G.; Jill, K. Tributyltin retards regeneration and produces deformities of limbs in the fiddler crab, *Uca pugilator*. *Arch. Environ. Contam. Toxicol.* **1987**, *16*, 321−326.
(18) Bryan, G. W.; Gibbs, P. E.; Hummerstone, L. G.; Burt, G. R. The decline of the gastropod *Nucella lapillus* around south-west England: Evidence for the effect of tributyltin from antifouling paints. *J. Mar. Assoc. U. K.* **1986**, *66*, 611−640.
(19) Aldis, O. V.; Bradley, M. D.; Peter, F. S. Sublethal growth effects and mortality to marine bivalves from long-term exposure to tributyltin. *Chemosphere* **1987**, *16*, 201−220.
(20) Karl, F. Ecotoxicology of organotins compounds. *Crit. Rev. Toxicol.* **1996**, *26*, 1−117.
(21) Jiang, G. B.; Zhou, Q. F. Direct Grignard pentylation of organotins-contamianted lard samples followed by capillary gas chromatography with flame photometric detection. *J. Chromatogr. A* **2000**, *886*, 197−205.
(22) Jiang, G. B.; Zhou, Q. F.; He, B. Speciation of organotin compounds, total tin, and major trace metal elements in poisoned human organs by gas chromatography-flame photometric detector and inductively coupled plasma-mass spectrometry. *Environ. Sci. Technol.* **2000**, *34*, 2697−2702.

Received for review April 3, 2001. Revised manuscript received June 26, 2001. Accepted June 27, 2001. This work was supported by the National Natural Science Foundation of China (29825114) and the Chinese Academy of Sciences (KZCX2-410, RCEES9902)

JF010438Y